

AN INFRARED STUDY OF THE CARBON-
NITROGEN DOUBLE BOND ABSORPTION
FREQUENCY IN SOME ALKYL AND ALKYL-
ARYL SUBSTITUTED SCHIFF'S BASES

By

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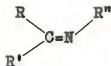
CHAPTER I

INTRODUCTION

Infrared studies of compounds containing carbon doubly bonded to carbon or to oxygen have established reasonably well the frequency ranges of the C=C and C=O absorptions and the frequency shifts to be expected with various substituents.^{2,19} The C-N has not been studied as thoroughly. In the C-N absorption Bellamy² quotes a frequency range of 1690 to 1640 cm^{-1} for open chain compounds and 1660 to 1630 cm^{-1} for alpha-beta unsaturated compounds. The assignments, however, are based primarily on compounds containing groups such as hydroxyl or amino which may influence the frequency.

Fabian, Legrand, and Poirier¹¹ reviewed the C-N frequencies of a variety of compounds reported in the literature and on the basis of somewhat limited data assigned frequency ranges for various classes of compounds and types of substitution.

The simplest class of C-N compounds are those having the structure



commonly called Schiff's bases. The ones having R' and R'' as an alkyl or aryl group and R as hydrogen atom or an alkyl group were chosen for study.

One notes from the preceding structure that these compounds can be considered as substituted nitrogen analogues of aldehydes and ketones. On this basis, one might predict that the various substituents represented by R and R' would influence the C-N stretching frequency in much the same way as substituents in similar positions influence the C=O stretching frequency. However, the C-N frequency should be subject to influences by the nitrogen substituent.

In addition to studying the sensitivity of the vibration toward various substituents, attention was paid to the remote possibilities of cis-trans isomerism and enamine-imine tautomerism. Kahovec^{16,17} concluded from Raman studies of some azomethines, Schiff's bases in which R represents hydrogen, that the compounds exist with R' and R'' in the trans positions. Hires and Balog¹⁴ attempted to convert N-butylidenebutylamine to a mixture of the two forms by a five to six hour exposure to

ultraviolet radiation, but no difference in the spectrum of the compound could be detected after irradiation. No indication of the presence of the two isomers appeared in any spectrum of the compounds studied in this investigation.

Bergmann, Zimkin, and Pinchas,³ in their study of factors favoring oxazolidene formation over Schiff's base formation when aldehydes or ketones are reacted with ethanolamine, postulated an enamine-imine tautomerism to explain an apparently anomalous absorption and studied additional compounds to support this conclusion. As will be discussed more fully in Chapter III, the results of this investigation indicate that infrared absorptions in themselves are not a reliable indication of such a tautomerism.

This study was undertaken in an attempt to assign frequency ranges for the C-N fundamental frequency in several classes of Schiff's bases and to correlate frequency changes with structural changes arising from the groups substituted on the carbon atom or on the nitrogen atom.

During the course of this investigation an extensive study of the C-N frequency in azomethines was published by Suydam.²¹ This work confirms his results within experimental error in all cases in which similar compounds were studied.

CHAPTER II

EXPERIMENTAL

Apparatus and Techniques

A Perkin-Elmer Model 21 double-beam, infrared spectrophotometer, linear in wavelength and per cent transmittance was used for this investigation. The instrument was equipped with a calcium fluoride prism and was calibrated according to the manufacturers instructions from 2.5 to 9.5 microns (4000 to 1050 cm^{-1}) using ammonia, methane and atmospheric water vapor. The tolerances for wavelength accuracy are ± 0.005 micron from 2.5 to 8.5 microns and ± 0.005 to ± 0.01 micron from 8.5 to 9.5 microns. The instrument was calibrated to within these tolerances. The corresponding accuracy in wavenumbers is $\pm 1\text{ cm}^{-1}$ in the region of primary concern, 1725 to 1640 cm^{-1} .

The slit program of 975 recommended by the manufacturer was used for all studies as well as for instrument calibration. This program gave a slit variation from 91 to 96 microns in the region 1725 to 1640 cm^{-1} and appeared to be the best compromise for low

noise, good response and adequate resolution. The amplifier gain and instrument zero were adjusted according to the manufacturers instructions.

A Perkin-Elmer Model 137 Infracord was used to record the qualitative spectra of all compounds investigated. All numerical data, however, were obtained by using the Model 21.

The spectra of the compounds as pure liquids were recorded from 2.5 to 9.5 microns using a 0.025 mm fixed cell. One compound, N-ethylidenemethylamine, boiled at room temperature, 25°C. Its spectrum was obtained in the gas phase using a 10 cm cell. The wavelengths of the C=N overtone were taken from these spectra.

The C=N absorption was measured in each case for the pure compound and for a CCl_4 solution. The band was recorded using a scale of 5 inches per micron at a speed of approximately 0.0004 microns per second. The wavelength of the peak was recorded from the instrument's counter reading. At least three measurements agreeing within 0.001 micron were taken for each compound.

The CCl_4 solutions were prepared in a 10 ml volumetric flask by weighing sample sufficient to give an absorption between 30 and 70 per cent transmission and diluting to volume. The more volatile samples were weighed

in a flask containing a small amount of CCl_4 to reduce loss by evaporation. The wavelength measurements were made using a 0.212 mm cell calibrated by the interference fringe method and the molar absorptivities calculated using Beer's law.

It was noted throughout the investigation that many of the compounds reacted with CCl_4 upon standing to produce a white, crystalline product. To reduce errors from this reaction the solutions were run within 30 minutes of preparation. The nature of the product is not known at this time although a reaction between triethylamine and CCl_4 producing an amine hydrochloride has been noted by Collins.⁶

The pure liquids, except N-ethylidenemethylamine measured in the gas phase, and N-methylene-tert-butylamine whose absorption was unusually weak, absorbed too strongly for accurate wavelength measurement using the smallest available fixed cell, 0.01 mm, and were too volatile to run directly between two sodium chloride plates. To overcome these difficulties, a simple demountable cell was assembled from the parts shown in Figure 1. The inside diameter of the teflon ring was made with a 1-degree taper to permit easy insertion and removal of the sodium chloride plates while still forming a tight seal.

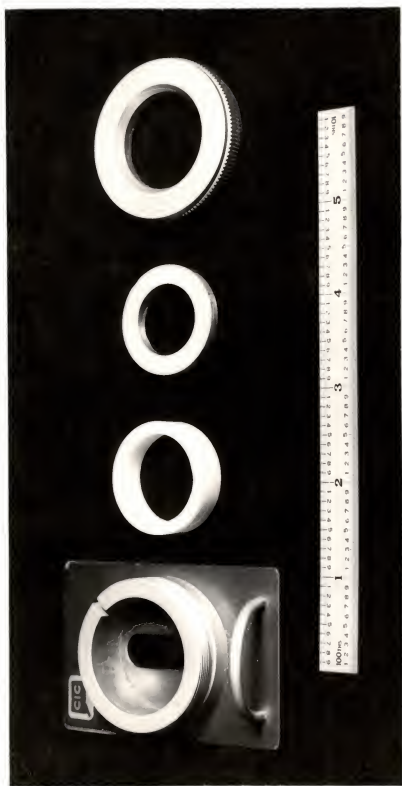
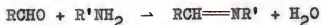


Fig. 1.-Demountable cell for pure liquids

Synthesis of Compounds

The compounds needed for this investigation were not available commercially and were, therefore, prepared by the following methods. All starting materials, unless otherwise indicated, were used as available from stock without further purification. Methylamine solution was prepared by dissolving the gas in water cooled externally by an ice bath.

The Schiff's bases produced by the reaction of an aldehyde and an amine, illustrated by the equation



were prepared as follows, according to the procedures of Campbell, Sommers and Campbell.⁵

Four-tenths mole of the amine was placed in a 250 ml, round-bottom, three-neck flask equipped with a reflux condenser, stirrer and addition funnel. The flask was surrounded by an ice bath, and 0.4 mole of aldehyde was added dropwise with stirring over a period of one to two hours. The reaction mixture was stirred for an additional 15 to 30 minutes after addition was completed. Solid KOH pellets were added and the mixture allowed to stand quietly until the removal of water seemed complete. The organic layer was separated, placed over a mixture of BaO

and crushed KOH, and refrigerated overnight. The material was decanted and purified by distillation from a small amount of BaO through a spinning band column.

Table 1 lists the compounds prepared by this method together with their boiling points experimentally measured during the course of this work as well as boiling points listed in the literature. All boiling points are uncorrected and at atmospheric pressure, unless otherwise indicated, in this and subsequent tables.

Figure 2 shows the apparatus used for the reactions as modified for the use of acetaldehyde. Circulation of ice water through the cold finger inserted into the addition funnel maintained acetaldehyde below its boiling point and permitted its addition without modification of the procedure.

It was found that the drying mixture of KOH and BaO was not completely effective in removing water from the compounds prepared from propionaldehyde, and the branched amines. For these compounds, it was necessary to dry over and distill from CaH_2 .

Ketones and amines undergo essentially the same reaction illustrated previously except that addition of an acid is necessary to catalyze the reaction.²² The following procedure, modified slightly from that of Norton²²

TABLE 1
COMPOUNDS PREPARED FROM ALDEHYDES AND AMINES

Aldehyde	Amine	Compound	Boiling Point °C	Boiling Point mm	Reported Boiling Point °C	Reported Boiling Point mm	Reference
HCHO	$(\text{CH}_3)_3\text{CNH}_2$	$\text{H}_2\text{C}=\text{NC}(\text{CH}_3)_3$	63		65	740	9
CH_3CHO	CH_3NH_2	$\text{CH}_3\text{CH}=\text{NCH}_3$	25		28-9	774	23
CH_3CHO	$\text{CH}_3\text{CH}_2\text{NH}_2^a$	$\text{CH}_3\text{CH}=\text{NCH}_2\text{CH}_3$	47.5		48	774	23
CH_3CHO	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$\text{CH}_3\text{CH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	74.5		74-5	760	23
CH_3CHO	$(\text{CH}_3)_2\text{CHNH}_2$	$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)_2$	61		58-9	754	23
CH_3CHO	$(\text{CH}_3)_3\text{CNH}_2$	$\text{CH}_3\text{CH}=\text{NC}(\text{CH}_3)_3$	81.3				
CH_3CHO	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$	87				
$\text{CH}_3\text{CH}_2\text{CHO}$	CH_3NH_2^a	$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}_3$	52		52.5	758	23
$\text{CH}_3\text{CH}_2\text{CHO}$	$\text{CH}_3\text{CH}_2\text{NH}_2^a$	$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}_2\text{CH}_3$	73		73.5	764	23
$\text{CH}_3\text{CH}_2\text{CHO}$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	97		101	760	23

^a Seventy per cent aqueous solution.

Table 1 (Continued)

Aldehyde	Amine	Compound	Boiling Point °C	Boiling Point mm	Reported Boiling Point °C	Reported Boiling Point mm	Reference
$\text{CH}_3\text{CH}_2\text{CHO}$	$(\text{CH}_3)_2\text{CHNH}_2$	$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}(\text{CH}_3)_2$	85		86-7	778	24
$\text{CH}_3\text{CH}_2\text{CHO}$	$(\text{CH}_3)_3\text{CNH}_2$	$\text{CH}_3\text{CH}_2\text{CH}=\text{NC}(\text{CH}_3)_3$	100				
$\text{CH}_3\text{CH}_2\text{CHO}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	110				
$(\text{CH}_3)_2\text{CHCHO}$	CH_3NH_2^a	$(\text{CH}_3)_2\text{CHCH}=\text{NCH}_3$	69		69.5	752	23
$(\text{CH}_3)_2\text{CHCHO}$	$\text{CH}_3\text{CH}_2\text{NH}_2^a$	$(\text{CH}_3)_2\text{CHCH}=\text{NCH}_2\text{CH}_3$	88		90	767	23
$(\text{CH}_3)_2\text{CHCHO}$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$(\text{CH}_3)_2\text{CHCH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	113		115.5	770	23
$(\text{CH}_3)_2\text{CHCHO}$	$(\text{CH}_3)_2\text{CHNH}_2$	$(\text{CH}_3)_2\text{CHCH}=\text{NCH}(\text{CH}_3)_2$	98		100	760	23
$(\text{CH}_3)_2\text{CHCHO}$	$(\text{CH}_3)_3\text{CNH}_2$	$(\text{CH}_3)_2\text{CHCH}=\text{NC}(\text{CH}_3)_3$	41.5	54	51-3	83	9
$(\text{CH}_3)_2\text{CHCHO}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$(\text{CH}_3)_2\text{CHCH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	43.4	43	124-5	772	23
$(\text{CH}_3)_2\text{CHCHO}$	$\text{C}_6\text{H}_5\text{NH}_2$	$(\text{CH}_3)_2\text{CHCH}=\text{NC}_6\text{H}_5$	48	1			

^aSeventy per cent aqueous solution.

Table 1 (Continued)

Aldehyde	Amine	Compound	Boiling Point °C	mm	Reported Boiling Point °C	mm	Refer- ence
$(\text{CH}_3)_3\text{CCHO}$	CH_3NH_2^a	$(\text{CH}_3)_3\text{CCH}=\text{NCH}_3$	81				
$(\text{CH}_3)_3\text{CCHO}$	$\text{CH}_3\text{CH}_2\text{NH}_2^a$	$(\text{CH}_3)_3\text{CCH}=\text{NCH}_2\text{CH}_3$	99				
$\text{C}_6\text{H}_5\text{CHO}$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	55	2	215		21

^aSeventy per cent aqueous solution.



Fig. 2.-Reaction vessel modified for addition of acetaldehyde

and his co-workers in the procedure of dehydration, was used to prepare the compounds listed in Table 2.

The ketone and amine, each in 0.4 molar amounts, were placed in a 500 ml glass-stoppered, Erlenmeyer flask and 1 ml of concentrated HCl was added dropwise. When necessary the flask was cooled under running water to prevent loss of reactants. The flask was loosely stoppered until cooled to room temperature and then tightly stoppered and allowed to stand at least 24 hours. KOH pellets were added and the mixture stirred magnetically until the KOH no longer seemed to dissolve. The organic layer was separated; fresh KOH was added; and the mixture was stirred as before. This process was repeated until water removal was complete. The product was then purified by distillation through a spinning band column.

The compounds prepared by Haury's method¹³ of reacting a Schiff's base with an amine boiling higher than the one originally used in preparation are listed in Table 3.

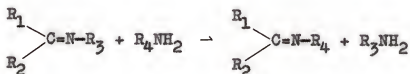


TABLE 2

SCHIFF'S BASES PREPARED BY DIRECT REACTIONS OF A KETONE AND AN AMINE

Ketone	Amine	Compound	Boiling Point °C	Boiling Point mm °C	Reported Boiling Point °C	Ref.
$(\text{CH}_3)_2\text{C}=\text{O}$	CH_3NH_2^a	$(\text{CH}_3)_2\text{C}=\text{NCH}_3$	63-4	65-6	65-6	4
$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{NH}_2$	$(\text{CH}_3)_2\text{C}=\text{NCH}_2\text{CH}_3$	83			
$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	$(\text{CH}_3)_2\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	104	107.2	107.2	22
$(\text{CH}_3)_2\text{C}=\text{O}$	$(\text{CH}_3)_2\text{CHNH}_2$	$(\text{CH}_3)_2\text{C}=\text{NCH}(\text{CH}_3)_2$	92	93.5	93.5	22
$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$(\text{CH}_3)_2\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	114			
$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{O}-\text{ClC}_6\text{H}_4\text{NH}_2$	$(\text{CH}_3)_2\text{C}=\text{N}(\text{O}-\text{ClC}_6\text{H}_4)$	54	1		
$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{m}-\text{ClC}_6\text{H}_4\text{NH}_2$	$(\text{CH}_3)_2\text{C}=\text{N}(\text{m}-\text{ClC}_6\text{H}_4)$	57-61	1		
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{O}$	CH_3NH_2^a	$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}_3$	89			
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{NH}_2$	$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}_2\text{CH}_3$	106			

^a Seventy per cent aqueous solution.

Table 2 (Continued)

Ketone	Amine	Compound	Boiling Point °C	Boiling Point mm	Reported Boiling Point °C	Ref.
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{O}$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	52.5	50	129.2	22
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{O}$	$(\text{CH}_3)_2\text{CHNH}_2$	$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}(\text{CH}_3)_2$	113		113.5	22
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$			134.5	22
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$	CH_3NH_2^a	$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}_3$	37.2	43		
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{NH}_2^a$	$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}_2\text{CH}_3$	46.5	37	52-4	54 9
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	63	43		
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	69	43		

^aSeventy per cent aqueous solution.

Table 2 (Continued)

Ketone	Amine	Compound	Reported		Ref.
			Bolling Point °C	Bolling Point mm °C	
$(C_6H_5)(CH_3)C=O$	$CH_3(CH_2)_2NH_2$	$(C_6H_5)(CH_3)C=N(CH_2)_2CH_3$	62	1	
$(O-ClC_6H_4)(CH_3)C=O$	$CH_3(CH_2)_2NH_2$	$(O-ClC_6H_4)(CH_3)C=N(CH_2)_2CH_3$	67	1	
$(m-ClC_6H_4)(CH_3)C=O$	$CH_3(CH_2)_2NH_2$	$(m-ClC_6H_4)(CH_3)C=N(CH_2)_2CH_3$	77	1	
$(p-ClC_6H_4)(CH_3)C=O$	$CH_3(CH_2)_2NH_2$	$(p-ClC_6H_4)(CH_3)C=N(CH_2)_2CH_3$	82	1	

^aSeventy per cent aqueous solution.

TABLE 3

COMPOUNDS PREPARED BY REACTING SCHIFF'S BASE WITH A PRIMARY AMINE

Schiff's Base	Amine	Compound	Boiling Point		Reported Boiling Pt.		Ref.
			°C	mm	°C	mm	
$(\text{CH}_3)_3\text{CCH=NCH}_3$	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$(\text{CH}_3)_3\text{CCH=N}(\text{CH}_2)_2\text{CH}_3$	44	42			
$(\text{CH}_3)_3\text{CCH=N}(\text{CH}_2)_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$	$(\text{CH}_3)_3\text{CCH=NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	47	44			
$(\text{CH}_3)_3\text{CCH=NCH}_2\text{CH}_3$	$(\text{CH}_3)_2\text{CHNH}_2$	$(\text{CH}_3)_3\text{CCH=NCH}(\text{CH}_3)_2$	107				
$(\text{CH}_3)_3\text{CCH=NCH}_2\text{CH}_3$	$(\text{CH}_3)_3\text{CNH}_2$	$(\text{CH}_3)_3\text{CCH=NC}(\text{CH}_3)_3$	37	35			
$(\text{CH}_3)_2\text{C=NCH}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{NH}_2$	$(\text{CH}_3)_2\text{C=NC}_6\text{H}_5$	82	15	129- 30	100	13

Equimolar amounts of Schiff's base and amine were refluxed in a spinning band column. Gaseous amine products were trapped in dilute HCl solution. When the amine product was a liquid, it was distilled off at such a rate that the distillation temperature varied no more than one degree from the boiling point of the amine. The reaction was complete when gas was no longer evolved or the boiling point could no longer be maintained. The products were then purified by distillation through the column.

Di-tert-butylketimine was synthesized according to the method generally outlined by Hansley.¹² The following equations illustrate the reactions:



Finely divided sodium was prepared in a 500 ml, three-neck, round-bottom flask by rapid stirring of 25.5 g of the metal in 100 ml of boiling xylene and allowing the mixture to cool. The xylene was decanted and the sodium washed three times with anhydrous ether. The sodium was placed under 325 ml of dry hexane and 67 g of trimethylacetone nitrile was added dropwise at room temperature with stirring over a period of about two hours. The reaction was completed by refluxing overnight. The

mixture was cooled to ice bath temperature, and an excess of water was added very slowly with stirring until all solid material had dissolved. The organic layer was separated and dried over KOH in a refrigerator for a period of 24 hours. Hexane was removed by distillation at atmospheric pressure through a spinning band column, and the product finally purified by distillation at reduced pressure, bp 71° at 34 mm; reported as 164-70° at atmospheric pressure.¹²

CHAPTER III

RESULTS AND DISCUSSION

The Schiff's bases studied containing non-aryl substituents on the carbon and nitrogen atoms are listed in Table 4, together with the fundamental C=N frequency, the overtone frequency, molar absorptivity, and the known literature values. Interference by the water vapor present in the atmosphere on the recorded spectra was noted frequently during the investigation as a false splitting of the fundamental C=N peak. The interference was reduced to a minimum by careful adjustment of the instrument and by keeping the maximum intensity between 30 and 70 per cent transmission. This interference is attributed to the high humidity conditions and the great dispersion of the calcium fluoride prism. Because of this interference, the values are considered accurate to $\pm 3 \text{ cm}^{-1}$ rather than the $\pm 1 \text{ cm}^{-1}$ which should be possible with the instrument. The overtone frequency is accurate to $\pm 10 \text{ cm}^{-1}$. Literature values quoted are for infrared measurements unless otherwise indicated and are considered to be accurate to no better than $\pm 6 \text{ cm}^{-1}$ corresponding to the calibrated accuracy of ± 0.02 microns generally

TABLE 4

SPECTRAL DATA FOR NON-ARYL SCHIFF'S BASES

Compound	Frequency in cm^{-1} Pure Compound Solution	Overtone Frequency in cm^{-1}	Molar Absorptivity ($\text{M}/\text{L}/\text{cm}$)	Literature Value
$\text{HN}=\text{C}[\text{C}(\text{CH}_3)_3]_2$	1605	3175	160	1673 ^{16,b}
$\text{CH}_3\text{N}=\text{CHCH}_3$	1695 ^a 1679 ^a	3342 ^a	160	1674 ^{16,b} 1673 ^{18,b}
$\text{CH}_3\text{N}=\text{CHCH}_2\text{CH}_3$	1678	3331	160	1667 ²¹ , 1673 ^{18,b}
$\text{CH}_3\text{N}=\text{CHCH}(\text{CH}_3)_2$	1678	3332	180	1668 ^{16,b}
$\text{CH}_3\text{N}=\text{CHC}(\text{CH}_3)_3$	1674	3322	220	1667 ²¹ , 1670 ¹⁸
$\text{CH}_3\text{N}=\text{C}(\text{CH}_3)_2$	1671	3315	240	
$\text{CH}_3\text{N}=\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$	1667	3310	150	
$\text{CH}_3\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2$	1667	3311	150	
$\text{CH}_3\text{CH}_2\text{N}=\text{CHCH}_3$	1675	3328	170	
$\text{CH}_3\text{CH}_2\text{N}=\text{CHCH}_2\text{CH}_3$	1673	3322	150	

^aGas phase.^bRaman.

Table 4 (Continued)

Compound	Frequency in cm ⁻¹ Pure Compound Solution	Overtone Frequency in cm ⁻¹	Molar Absorptivity (M ^{1/2} /cm)	Literature Value
CH ₃ CH ₂ N=CHCH(CH ₃) ₂	1674	3320	190	1669 ²¹
CH ₃ CH ₂ N=CHC(CH ₃) ₃	1669	3306	200	
CH ₃ CH ₂ N=C(CH ₃) ₂	1667	3312	240	
CH ₃ CH ₂ N=C(CH ₃)(CH ₂ CH ₃)	1661	3310	140	1660 ⁹
CH ₃ CH ₂ N=C(CH ₂ CH ₃) ₂	1661	3300	140	1671 ^{16, b}
CH ₃ (CH ₂) ₂ N=CHCH ₃	1675	3328	180	1667 ²¹
CH ₃ (CH ₂) ₂ N=CHCH ₂ CH ₃	1674	3323	200	1673 ¹⁰
				1670 ^{16, b}
				1669 ²¹
CH ₃ (CH ₂) ₂ N=CHCH(CH ₃) ₂	1674	3327	200	
CH ₃ (CH ₂) ₂ N=CHC(CH ₃) ₃	1671	3311	180	
CH ₃ (CH ₂) ₂ N=C(CH ₃) ₂	1668	3313	190	

^aGas phase.^bRaman.

Table 4 (Continued)

Compound	Frequency in cm^{-1} Pure Compound	Frequency in cm^{-1} Solution	Overtone Frequency in cm^{-1}	Molar Absorptivity ($\text{M}/\text{l}/\text{cm}$)	Literature Value
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$	1668	1661	3307	150	
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2$	1665	1661	3306	150	
$(\text{CH}_3)_2\text{CHN}=\text{CHCH}_3$	1679	1678	3320	140	1664 ²¹ 1672 ^{16, a} 1677 ²⁰
$(\text{CH}_3)_2\text{CHN}=\text{CHCH}_2\text{CH}_3$	1669	1669	3317	160	1672 ²¹
$(\text{CH}_3)_2\text{CHN}=\text{CHCH}(\text{CH}_3)_2$	1669	1669	3317	200	
$(\text{CH}_3)_2\text{CHN}=\text{CHC}(\text{CH}_3)_3$	1666	1666	3311	210	
$(\text{CH}_3)_2\text{CHN}=\text{C}(\text{CH}_3)_2$	1666	1666	3317	310	
$(\text{CH}_3)_2\text{CHN}=\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$	1661	1659	3309	170	
$(\text{CH}_3)_2\text{CHN}=\text{C}(\text{CH}_2\text{CH}_3)_2$	1661	1660	3311	140	
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN}=\text{CHCH}_3$	1675	1674	3322	180	1664 ²¹

^aGas phase.^bRaman.

Table 4 (Continued)

Compound	Frequency in cm ⁻¹ Pure Compound	Frequency in cm ⁻¹ Solution	Overtone Frequency in cm ⁻¹	Molar Absorptivity (M/l/cm)	Literature Value
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-CHCH}_2\text{CH}_3$	1674	1674	3318	140	1667 ²¹
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-CHCH}(\text{CH}_3)_2$	1669	1669	3314	200	1669 ²¹ 1670 ⁹
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-CHC}(\text{CH}_3)_3$	1667	1667	3312	230	
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-C}(\text{CH}_3)_2$	1668	1666	3320	240	
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$	1662	1660	3309	160	
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHN-C}(\text{CH}_2\text{CH}_3)_2$	1662	1660	3311	160	
$(\text{CH}_3)_3\text{CN-CHCH}_3$	1675	1672	3323	170	
$(\text{CH}_3)_3\text{CN-CHCH}_2\text{CH}_3$	1674	1673	3323	140	
$(\text{CH}_3)_3\text{CN-CHCH}(\text{CH}_3)_2$	1675	1674	3328	120	
$(\text{CH}_3)_3\text{CN-CHC}(\text{CH}_3)_3$	1666	1666	3312	120	
$(\text{CH}_3)_3\text{CN-CH}_2$	1653	1653	-	21	

^aGas phase.^bRaman.

attainable by sodium chloride prisms. The accuracy of the Raman data is unknown. Since molar absorptivities depend upon the condition of the instrument at the time the measurement is made and vary from instrument to instrument, they were not determined more accurately than ± 10 per cent.

In general the determined frequencies are higher than those reported previously for the same compounds. The Raman data reported by Kahovec¹⁶ and by Kirrmann and Laurent¹⁸ for several of the compounds studied in this investigation are consistently lower by 5 cm^{-1} than the data determined by the author. This difference is attributed to the different methods of measurement. The reported frequency value of 1666 cm^{-1} for N-ethylidene-methylamine is believed to be in error since this value is inconsistent with the C=N frequencies of structurally similar compounds. The infrared data of Suydam²¹ generally agree within the $\pm 10\text{ cm}^{-1}$ * expected in this region when comparing data obtained with sodium chloride and calcium fluoride prisms.

* This includes the $\pm 6\text{ cm}^{-1}$ error in wavelength calibration and the $\pm 3\text{ cm}^{-1}$ error in reproducibility for sodium chloride, plus the $\pm 1\text{ cm}^{-1}$ error in calcium fluoride calibration.

The frequencies resulting from different combinations of alkyl substituents on the carbon and nitrogen atoms are shown in Table 5. The values measured for pure liquids appear above the diagonal, and those measured in solution and the calculated absorptivities appear below.

The azomethines, $RCH=NR'$, were found to have a slightly greater frequency range, 1680 to 1665 cm^{-1} , than reported previously.^{11,21} If the compounds containing an isopropyl group are excluded, the general trends of the C=N frequencies shown in Table 5 are (1) a slight drop of about 4 cm^{-1} when R represents a tert-butyl group and R' is unbranched, and (2) a drop of about the same magnitude for a given R group when R' is a substituent other than a methyl group. An isopropyl group substituted on the carbon atom follows the trend indicated for the other R groups as R' is varied until combined with itself or with a sec-butyl group. A drop in frequency occurs when either of these two groups is substituted on the nitrogen atom, and a rise in frequency occurs when a tert-butyl group is the nitrogen substituent.

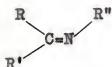
Further anomalous behavior occurs when the isopropyl group is R'. Comparison of the values for the isopropyl group when combined with a methyl or an ethyl group with those obtained for a sec-butyl or tert-butyl group in the same combination shows an unusually high and low value,

TABLE 5
C=N FREQUENCIES AND ABSORPTIVITIES FOR VARIOUS
COMBINATIONS OF SUBSTITUENTS

$\begin{array}{c} \text{O} \\ \diagdown \\ \text{N} \end{array}$	H CH ₃	H CH ₃ CH ₂	H (CH ₃) ₂ CH	H (CH ₃) ₃ C	CH ₃ CH ₃	CH ₃ CH ₃ CH ₂	CH ₃ CH ₂ CH ₃ CH ₂
CH ₃	1679 $\frac{1679}{160}$	1678 $\frac{1678}{160}$	1678 $\frac{1678}{180}$	1674 $\frac{1674}{220}$	1671 $\frac{1672}{240}$	1667 $\frac{1667}{150}$	1667 $\frac{1667}{150}$
CH ₃ CH ₂	1675 $\frac{1675}{170}$	1673 $\frac{1672}{150}$	1674 $\frac{1672}{190}$	1669 $\frac{1669}{200}$	1667 $\frac{1666}{240}$	1661 $\frac{1661}{140}$	1661 $\frac{1661}{140}$
CH ₃ (CH ₂) ₂	1675 $\frac{1675}{180}$	1674 $\frac{1674}{200}$	1674 $\frac{1673}{200}$	1671 $\frac{1671}{180}$	1668 $\frac{1667}{190}$	1668 $\frac{1661}{150}$	1665 $\frac{1661}{150}$
(CH ₃) ₂ CH	1679 $\frac{1678}{140}$	1669 $\frac{1669}{160}$	1669 $\frac{1669}{200}$	1666 $\frac{1666}{210}$	1666 $\frac{1666}{310}$	1661 $\frac{1659}{170}$	1661 $\frac{1660}{150}$
CH ₃ CH ₂ (CH ₃)CH	1675 $\frac{1674}{180}$	1674 $\frac{1674}{140}$	1669 $\frac{1669}{200}$	1667 $\frac{1667}{230}$	1668 $\frac{1666}{240}$	1662 $\frac{1660}{160}$	1662 $\frac{1660}{160}$
(CH ₃) ₃ C	1675 $\frac{1672}{170}$	1674 $\frac{1673}{140}$	1675 $\frac{1674}{120}$	1666 $\frac{1666}{120}$			

respectively. Even if one assumes that the value for the isopropyl-methyl combination should be about 3 cm^{-1} lower, the low value obtained when R is an ethyl group still seems inconsistent. However, resynthesis of the compound and remeasurement of the frequency confirms the value. No explanation for the behavior of the isopropyl group can be set forth at this time. The close agreement between the solution and pure liquid frequencies seems to indicate that the behavior is not due to an intermolecular interaction.

The Schiff's bases of the structure absorb at a



lower frequency range, 1672 to 1660 cm^{-1} , than the azomethines. This is much higher than the range of 1662 to 1649 cm^{-1} quoted by Fabian, Legrand, and Poirier¹¹ based on compounds containing the hydroxyethyl group on the nitrogen. The infrared data reported by Emmons⁹ for four compounds similar to those studied fall within the quoted range.

The trends in the data are similar and slightly more regular than with the azomethines. A drop in frequency occurs for a given R" when R and R' are not

both methyl groups. When R" is different from methyl, the frequency drops to essentially the same value for a given combination of R and R'. The difference between the liquid and solution frequencies of N-sec-butylidenepropylamine and N-2-pentylidenepropylamine is attributed to the greater intermolecular interaction possible in the liquid state. Attempts to prepare the compounds having the tert-butyl group as R" by the methods described in Chapter II were unsuccessful. Molecular models indicate that there is little space for such a large group on the nitrogen atom.

The molar absorptivities listed in Table 5 range in value from 120 to 310 M/l/cm and do not seem to show any well defined trends except in the case of the Schiff's base analogues of ketones. The ketone analogues have molar absorptivities comparable in magnitude to those values quoted by Bellamy² for ketones and have roughly the same trend as the frequencies, namely, a decrease in value when one or both methyl groups is replaced by an ethyl group.

The range of absorptivities tabulated and the number of compounds represented suggested that the application of elementary statistics to the grouping of the data might reveal some general effects of the substituents.

The number of intervals or classes needed to group the data was estimated by the following equation¹⁵ in which "k" represents the number of intervals and "n" represents the number of values comprising the data:

$$k = 1 + 3.3 \log_{10} n .$$

By combining the value obtained from the equation with the range of the data, it was determined that seven intervals of 30 units were needed. The result of the grouping is shown graphically by the frequency polygon, Figure 3, obtained by plotting the statistical frequency, the number of values in each interval, against the midpoint of the interval.

The compounds are classified according to absorptivity interval and decreasing absorptivities within the interval in Table 6. The compounds having two methyl groups on the carbon atom in general show the highest intensities, and these further seem to be dependent on the branched nature of the group substituted on the nitrogen atom as shown by the comparison of the values for the isopropyl and sec-butyl groups.

Comparison of the azomethines having absorptivities between 210 and 240 M/l/cm with those having absorptivities between 120 and 150 M/l/cm reveals one alkyl group, the tert-butyl, common to both intervals. In general, the

TABLE 6
INTERVAL GROUPINGS OF THE SCHIFF'S BASES ACCORDING
TO THEIR ABSORPTIVITY VALUES

Compound	Molar Absorptivity (M/l/cm)
Interval 300-329	
$(\text{CH}_3)_2\text{C}=\text{NCH}(\text{CH}_3)_2$	310
Interval 270-299	
None	
Interval 240-269	
$(\text{CH}_3)_2\text{C}=\text{NCH}_3$	240
$(\text{CH}_3)_2\text{C}=\text{NCH}_2\text{CH}_3$	240
$(\text{CH}_3)_2\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	230
Interval 210-239	
$(\text{CH}_3)_3\text{CCH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	230
$(\text{CH}_3)_3\text{CCH}=\text{NCH}_3$	220
$(\text{CH}_3)_3\text{CCH}=\text{NCH}(\text{CH}_3)_2$	210

Table 6 (Continued)

Compound	Molar Absorptivity (M/l/cm)
Interval 180-209	
$(\text{CH}_3)_3\text{CCH}=\text{NCH}_2\text{CH}_3$	200
$(\text{CH}_3)_2\text{CHCH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	200
$(\text{CH}_3)_2\text{CHCH}=\text{NCH}(\text{CH}_3)_2$	200
$(\text{CH}_3)_2\text{CHCH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	200
$(\text{CH}_3)_2\text{CHCH}=\text{NCH}_2\text{CH}_3$	190
$(\text{CH}_3)_2\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	190
$(\text{CH}_3)_2\text{CHCH}=\text{NCH}_3$	180
$(\text{CH}_3)_3\text{CCH}=\text{N}(\text{CH}_2)_2\text{CH}_3$	180
$\text{CH}_3\text{CH}=\text{N}(\text{CH}_2)_3\text{CH}_3$	180
$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	180
Interval 150-179	
$\text{CH}_3\text{CH}=\text{NCH}_2\text{CH}_3$	170
$\text{CH}_3\text{CH}=\text{NC}(\text{CH}_3)_3$	170
$\text{CH}_3\text{CH}=\text{NCH}_3$	160
$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}_3$	160
$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}(\text{CH}_3)_2$	160
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	160
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	160

Table 6 (Continued)

Compound	Molar Absorptivity (M/L/cm)
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Interval 150-179 continued

$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}_2\text{CH}_3$	150
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}_3$	150
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	150
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}_3$	150
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{N}(\text{CH}_2)_2\text{CH}_3$	150
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}(\text{CH}_3)_2$	150
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	150

Interval 120-149

$\text{CH}_3\text{CH}=\text{NCH}(\text{CH}_3)_2$	140
$\text{CH}_3\text{CH}_2\text{CH}=\text{NC}(\text{CH}_3)_3$	140
$\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	140
$(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{C}=\text{NCH}_2\text{CH}_3$	140
$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NCH}_2\text{CH}_3$	140
$(\text{CH}_3)_2\text{CHCH}=\text{NC}(\text{CH}_3)_3$	120
$(\text{CH}_3)_2\text{CHCH}=\text{NC}(\text{CH}_3)_3$	120

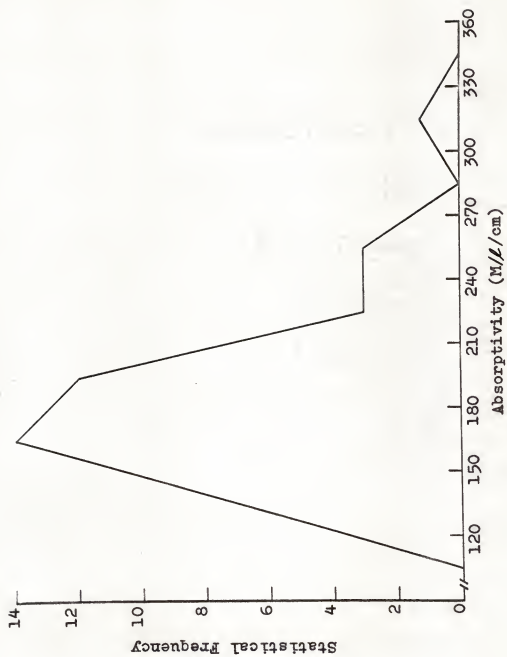


Fig. 3.-Frequency Polygon

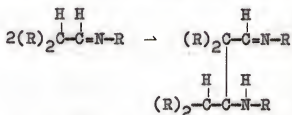
tert-butyl group produces an extreme enhancement when substituted on the carbon atom and an opposite effect when substituted on the nitrogen atom.

In addition to their use in quantitative analysis, absorptivities may be considered qualitatively as a measure of the detectability of a particular functional group. The dependence of molar absorptivity on frequency allows only a general comparison. A much better comparison of the inherent absorption of a specific group is possible with integrated intensities. Unfortunately, instruments which plot the function of absorbancy versus frequency needed for convenient integration are not readily available.

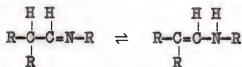
An unexpected result was the consistent appearance of a peak in the region of 3300 cm^{-1} which is attributed to the first overtone of the C=N fundamental. The assignment of this peak is of some importance since peaks in this region have been quoted as evidence of enamine-imine tautomerism.^{3,25} An absorption in the vicinity of 3300 cm^{-1} is usually attributed to an N-H stretching frequency and is considered as evidence of an N-H grouping. For the compounds investigated, an N-H group may arise in three possible ways. First, some of the amine starting material may not have been completely separated from the

product. The constancy of the boiling point and the lack of the two peaks associated with the NH_2 absorption of the amine seemed to rule out this possibility. Vapor phase chromatography gave no evidence of the presence of the amine starting material.

The second way an N-H group can arise is by the compounds undergoing the following dimerization similar to that postulated by Emerson, Hess, and Uhle.⁸



A third possibility is that the Schiff's base may exist in the following tautomeric equilibrium.



The latter two possibilities require the presence of a hydrogen atom on the carbon alpha to the double bond. As can be seen in Table 4, those compounds having no hydrogen in this position still show an absorption in the 3300 cm^{-1} region which can only be attributed to the first overtone of the C=N fundamental stretching frequency. The overtone frequency also follows the same general trends as

the fundamental and, as expected for overtone frequencies, is always slightly less than twice the fundamental.

Table 7 lists the Schiff's bases having an aryl or a chloro-substituted aryl group on the doubly bonded carbon atom. As would be expected, the phenyl group causes a marked lowering of the frequency for the azo-methines. Substitution of an alkyl group for the hydrogen attached to the carbon produces a further decrease in frequency which is consistent with the behavior found in the case of the totally alkyl substituted compounds.

Chlorine substitution at the ortho or para position does not produce the further lowering of the C=N frequency which one might predict on the basis of the following resonance structures:

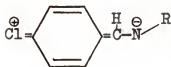
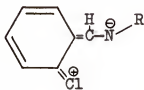


TABLE 7
SPECTRAL DATA FOR CARBON SUBSTITUTED ALKYL-ARYL SCHIFF'S BASES

Compound	Frequency in cm^{-1} Pure Liquid	Frequency in cm^{-1} Solution	Overtone Frequency in cm^{-1}	Molar Absorptivity ($\text{M}/\ell/\text{cm}$)	Literature Value
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{CHC}_6\text{H}_5$	1647	1649	3274	320	1650 ²⁰
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)$	1634	1634	3254	140	
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(\text{o-ClC}_6\text{H}_4)$	1657	1657	3287	190	
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(\text{m-ClC}_6\text{H}_4)$	1637	1637	3249	160	
$\text{CH}_3(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(\text{p-ClC}_6\text{H}_4)$	1634	1634	3250	150	

The inductive effect of the chlorine in the para position apparently raises the frequency sufficiently to overcome the lowering expected from the above contribution, and as a consequence, the absorption frequency is about the same as the unsubstituted compound.

The high frequency of the ortho substituted compound can be accounted for in two ways. Figure 4 shows a molecular model with the N-1-methyl-o-chlorobenzylidene-propylamine with the chlorophenyl group and the C=N in a planar configuration. In this position the field effect postulated by Bellamy² to explain the shift to higher frequency for alpha-chloro substituted acetones, mutual induction of opposite charges in the chlorine and oxygen reducing the polarity of the C=O, could cause a rise in frequency. Secondly, rotation of the ring from the plane of the double bond, presumably caused by the mutual repulsion of the chlorine's electrons and the nitrogen's lone pair, can reduce the conjugation and shift the frequency upward.

Of the two possibilities the latter seems most likely although both effects may be operating simultaneously. Bergmann, Zimkin, and Pinchas³ report frequencies of 1633 cm^{-1} for N-1-methylbenzylidene cyclohexylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{C}=\text{NC}_6\text{H}_{11}$, and 1650 cm^{-1} for N-1-methyl-o-methylbenzylidene cyclohexylamine (o- $\text{CH}_2\text{C}_6\text{H}_4$)(CH_3) $\text{C}=\text{NC}_6\text{H}_{11}$.



Fig. 4.-Molecular model for the planar form of N-1-methyl-o-chlorobenzylidene-propylamine

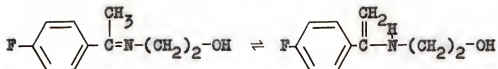
The 17 cm^{-1} difference comparable in magnitude to the 23 cm^{-1} for the o-chloro substitution supports this conclusion since a methyl group would not be expected to show a field effect.

A similar ortho effect does not seem to be observed for azomethines. Daasch and Hanninen⁷ quote values of 1645 cm^{-1} and 1640 cm^{-1} for N-(2-hydroxyethyl)-benzalamine, $\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{CH}_2)_2\text{OH}$ and N-(2-hydroxyethyl)-2-chlorobenzalamine, o-ClC₆H₄CH=N(CH₂)₂OH, respectively. Figure 5 shows the interference of the methyl group with the rotation of the o-chlorophenyl substituent. This prevents the ortho position orientating cis to the nitrogen group. Manipulation of the models with a hydrogen in place of the methyl indicates that the steric hindrance to rotation no longer exists permitting a planar configuration and producing the similar reported values.

The overtone frequency is also present in these compounds and follows the same trend in general as does the fundamental. Bergmann³ and his co-workers attribute an otherwise unexplained peak at 1682 cm^{-1} for N-1-methyl-p-fluorobenzylidene hydroxyethylamine (p-FC₆H₄)(CH₃)C=N(CH₂)₂OH, to the following enamine-imine tautomerism.

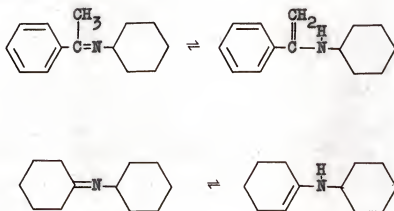


Fig. 5.-Molecular model of N-1-methyl-0-chlorobenzylidenepropylamine showing hindered rotation of phenyl group



They noted also that alpha-methylstyrene has a similar peak at 1690 cm^{-1} .

To further substantiate the tautomerism, Bergmann and co-workers prepared the compounds and obtained the infrared data listed in Table 8. It was concluded on the basis of the 1693 cm^{-1} peak of compound 1, the 2770 and 2840 peaks of compound 3 which were compared with similar peaks at 2781 and 2824 cm^{-1} * in cyclohexene, and the peaks for both compounds in the 3000 cm^{-1} region that each of the two compounds exists in equilibrium with its tautomer as shown:



*Reference 1, serial number 697 lists these peaks but inspection of the accompanying spectrum shows little evidence for their presence. Serial number 201 of reference 1 for the same compound does not list an absorption at these positions nor does the spectrum reveal any nearby.

TABLE 8
INFRARED ABSORPTION DATA FOR COMPOUNDS REPORTED TO EXIST AS ENAMINE-IMINE TAUTOMERS³

Compound	Absorption Frequencies in cm ⁻¹		
	C=N Region	C-H Region	N-H Region
1. $(C_6H_5)(CH_3)C=NC_6H_{11}$	1633	2770 2840	3190
2. $(O-CH_3C_6H_4)(CH_3)C=NC_6H_{11}$	1650		3420
3. $H_2C(CH_2)_4C=NC_6H_{11}$	1649		3240
4. $C_6H_5CH=NC_6H_5$	1642		

On the basis of the weak "NH" absorption and the absence of a peak at about 1690 cm^{-1} the equilibrium of compound 2 was assumed to be displaced largely toward the imine form due to the ortho methyl group.

All the peaks reported can be interpreted differently. The 1690 cm^{-1} absorptions of compounds 1 and 3 and the lack thereof in compound 2 can be correlated with the overtone-combination peaks characteristic of an aromatic group. Uncorrelated peaks often appear in the 2700 cm^{-1} region. The frequencies near 3000 cm^{-1} may of course be overtones although the absence of such an absorption for compound 4 cannot be explained and is unusual when compared with the compound in Table 7 differing only in a propyl group instead of a cyclohexyl.

There were no peaks appearing in any of the compounds studied which would lend support to such a tautomerism. This does not exclude, however, the possibility but only indicates that the concentration may be too low to detect. Since the existence of an overtone which might easily be confused with an N-H stretching vibration has been demonstrated, due caution should be exercised when quoting an absorption in this region as evidence of tautomerism even in cases where it may reasonably be expected to exist.²⁵

Table 9 lists the data for compounds in which a phenyl or chloro-substituted phenyl group is attached to the nitrogen. The azomethine shows a drop in frequency as might be expected showing that conjugation can occur through the nitrogen as well as through the carbon. The dimethyl substitution on the carbon atom of the double bond raises the frequency to that shown by the N-alkyl substituted compounds listed in Table 5. The molecular model of N-isopropylidene-p-chloroaniline, Figure 6, shows that the presence of two methyl groups prevents the phenyl group from attaining sufficient planarity for conjugation, hence the rise in frequency. Further evidence for this configuration comes from the infrared absorption of the C-N vibration which is expected to occur between 1360 and 1310 cm^{-1} for aromatic amines due to the partial double bond character of the linkage. The absorption peak due to the C-N split into a doublet at about 1235 cm^{-1} in the region expected for aliphatic amines and is almost identical in position with the C-N frequencies of the similar N-alkyl substituted compounds. The C-N frequencies for both the N-alkyl and N-aryl compounds are listed for comparison in Table 10.

TABLE 9
SPECTRAL DATA FOR ARYL NITROGEN SUBSTITUTED SCHIFF'S BASES

Compound	Frequency in cm^{-1} Pure Compound	Solution	Overtone Frequency in cm^{-1}	Molar Absorptivity ($\text{M}/\ell/\text{cm}$)
$\text{C}_6\text{H}_5\text{N}=\text{CHCH}(\text{CH}_3)_2$	1652	1657	a	210
$\text{C}_6\text{H}_5\text{N}=\text{C}(\text{CH}_3)_2$	1666	1666	3312	210
$\text{o}-\text{ClC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2$	1668	1671	a	330
$\text{m}-\text{ClC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2$	1669	1671	a	350

^aHidden by residual amine.

TABLE 10
C-N STRETCHING FREQUENCIES OF DIMETHYL SUBSTITUTED
SCHIFF'S BASES

Compound	C-N Frequencies in cm^{-1}	
$\text{CH}_3\text{N}=\text{C}(\text{CH}_3)_2$	1248	
$\text{CH}_3\text{CH}_2\text{N}=\text{C}(\text{CH}_3)_2$	1239	
$(\text{CH}_3)_2\text{CHN}=\text{C}(\text{CH}_3)_2$	1238	
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{N}=\text{C}(\text{CH}_3)_2$	1232	
$\text{C}_6\text{H}_5\text{N}=\text{C}(\text{CH}_3)_2$	1241	1228
$\text{o-ClC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2$	1245	1221
$\text{m-ClC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2$	1241	1224



Fig. 6.-Molecular model of N-isopropylideneaniline

Further study of the model shown in Figure 6 reveals that if the compound existed in this configuration, it would have an enantiomorph by virtue of the ortho substitution. Resolution of this or other similar compounds having ortho or meta substitution would lend further support to the configuration.

CHAPTER IV

SUMMARY

Schiff's bases, having various combinations of substituents, were synthesized, and the C=N stretching frequencies were measured for the compounds as pure liquids and as CCl_4 solutions. The molar absorptivities of the C=N absorption were also calculated as a quantitative indication of the intensity of the absorption.

The C=N stretching frequencies for the azomethines containing only alkyl groups on the nitrogen and carbon atoms were found to be in the wavenumber range from 1680 to 1666 cm^{-1} . Substitution of a phenyl group on the nitrogen or carbon atom lowered the frequency through conjugation to 1650 cm^{-1} .

The C=N stretching frequency of the Schiff's bases classifiable as N-substituted ketimines were in the wavenumber range from 1672 to 1660 cm^{-1} for the compounds having only alkyl substituents. Unlike the case of the azomethines, an aryl substituent on the carbon or nitrogen atom in the ketimine compounds did not produce the same frequency effect. Aryl substitution for one of the alkyl groups attached to the carbon lowered the

frequency by conjugation with the C=N. Steric factors influenced the extent of the lowering when the phenyl ring was substituted in the ortho position. Substitution of an alkyl group on the nitrogen atom by an aryl group did not produce any significant change in the C=N stretching frequency because conjugation was inhibited by the alkyl group in the cis position.

A weak absorption in the 3300 cm^{-1} region occurring in all spectra of the compounds studied, including those compounds in which tautomerization could not occur, was assigned as an overtone of the C=N vibration.

The molar absorptivities ranged from 120 to 230 M/l/cm for the azomethines, 150 to 310 M/l/cm for the N-alkyldialkyl ketimines, 210 to 350 M/l/cm for N-aryldialkyl ketimines, and 140 to 190 M/l/cm for N-alkylarylalkyl ketimines.

BIBLIOGRAPHY

1. American Petroleum Institute Project 44. "Infrared Spectral Data."
2. Bellamy, L. J., "The Infrared Spectra of Complex Molecules." Second Edition, John Wiley and Sons, Inc., New York (1958).
3. Bergmann, Ernst D., Zimkin, E., and Pinchas, S., Rec. Trav. Chim., 71, 168-9 (1952).
4. Blomberg, Richard N. and Bruce, William F., U. S. Patent 2,700,681 (Jan. 25, 1955).
5. Campbell, Kenneth N., Sommers, Armiger H., and Campbell, Barbara K., J. Am. Chem. Soc., 66, 82-4 (1944).
6. Collins, R. F., Chem. Ind. (London), 1957, 704.
7. Daasch, L. W. and Hanninen, Urho E., J. Am. Chem. Soc., 72, 3673-6 (1950).
8. Emerson, William S., Hess, S. M., and Uhle, F. C., J. Am. Chem. Soc., 63, 872 (1941).
9. Emmons, William D., J. Am. Chem. Soc., 79, 5739-54 (1957).
10. Fabian, Joyce and Legrand, Maurice, Bull. Soc. Chim. France, 1956, 1461-3.
11. Fabian, Joyce, Legrand, Maurice, and Poirier, Pierre, Bull. Soc. Chim. France, 1956, 1499-1509.
12. Hansley, Virgil L., U. S. Patent 2,742,503 (Apr. 17, 1956).
13. Haury, Vernon E., U. S. Patent 2,513,996 (July 4, 1950).
14. Hires, J. and Balog, J., Acta Univ. Szegediensis, Acta Phys. et Chem. [N.S.], 2, 87-94 (1956).

15. Huntsberger, David V., "Elements of Statistical Inference." Allyn and Bacon, Inc., Boston (1961).
16. Kahovec, L., Acta Phys. Austriaca, 1, 307-16 (1948).
17. Kahovec, L., Z. Physik. Chem. (Leipzig), B43, 364-74 (1939).
18. Kirrmann, A. and Laurent, P., Bull. Soc. Chim. France, 6, 1657-63 (1939).
19. Pijanowski, Leon S., Dissertation, University of Florida (1963).
20. Snyder, H. R. and Matteson, D. S., J. Am. Chem. Soc., 79, 2217-21 (1957).
21. Suydam, Fred H., Anal. Chem., 35, 193-5 (1963).
22. Norton, Douglas G., Haury, Vernon E., Davis, Frank C., Mitchell, Lloyd J., and Ballard, Seaver A., J. Org. Chem., 19, 1054-66 (1954).
23. Tiollais, Rene, Bull. Soc. Chim. France, 1947, 708-13.
24. Tiollais, Rene and Guillermin, Henri, Bull. Soc. Chim. France, 1953, 937-9.
25. Witkop, Bernhard, J. Am. Chem. Soc., 78, 2873-82 (1956).

BIOGRAPHICAL SKETCH

William Leroy Steele was born August 1, 1932, at Alliance, Ohio. In June, 1950, he was graduated from the Alliance High School.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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